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13. ABSTRACT (Maximum 200 Words) To address the cost and performance barriers which hinder the introduction of composite materials for combat ground vehicle applications, Co-Injection Resin Transfer Molding (CIRTM) and Diffusion Enhanced Adhesion (DEA) have been recently invented and developed at the Army Research Laboratory and the University of Delaware. When applied in tandem, these two composite processing technologies enable the manufacture of lightweight composite/ceramic integral armor offering significant cost-reduction and performance enhancement over existing defense industry practices. CIRTM was invented and developed for single-step manufacturing of integral armor by enabling simultaneous injection of multiple resins into multi-layer preform. Several technical challenges exist that must be addressed to fully realize the benefits afforded by the CIRTM process. First, the ability to separate the different resins during processing while achieving excellent bonding between the layers is an important aspect of the CIRTM process. DEA has been shown to be an effective approach. Also, an understanding of the resin flow and cure kinetics will aid in process optimization. This paper introduces the CIRTM process and describes in detail the DEA approach for separation of the layers. A guide to materials selection is presented, practical examples of the process are discussed, and mechanical performance data is reviewed.							
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Co-Injection Resin Transfer Molding for Optimization of Integral Armor

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Abstract

To address the cost and performance barriers which hinder the introduction of composite materials for combat ground vehicle applications, Co-Injection Resin Transfer Molding (CIRTM) and Diffusion Enhanced Adhesion (DEA) have been recently invented and developed at the Army Research Laboratory and the University of Delaware. When applied in tandem, these two composite processing technologies enable the manufacture of lightweight composite/ceramic integral armor offering significant cost-reduction and performance enhancement over existing defense industry practices. CIRTM was invented and developed for single-step manufacturing of integral armor by enabling simultaneous injection of multiple resins into a multi-layer preform. Several technical challenges exist that must be addressed to fully realize the benefits afforded by the CIRTM process. First, the ability to separate the different resins during processing while achieving excellent bonding between the layers is an important aspect of the CIRTM process. DEA has been shown to be an effective approach. Also, an understanding of the resin flow and cure kinetics will aid in process optimization. This paper introduces the CIRTM process and describes in detail the DEA approach for separation of the layers. A guide to materials selection is presented, practical examples of the process are discussed, and mechanical performance data is reviewed.

1. Introduction

Current and developing Army applications have identified the need for lightweight structural materials in order to enhance deployability and increase mobility. Several research and development programs have demonstrated the effectiveness of composite materials for combat ground vehicles to meet these needs. Recent advances include the development of composite/ceramic integral armor systems (Composite Armored Vehicle – CAV-ATD) which provide significant improvement over previously used monocoque composite armor structures (Composite Infantry Fighting Vehicle). The integral armor concept employs different resin systems through the thickness of the structure to provide multi-functional capabilities (Figure 1a). These layers include an epoxy resin for structural performance, a phenolic resin for fire, smoke, and toxicity (FST) protection, and an elastomer for tile-composite shear load transfer. The manufacture of composite armor components currently involves multiple manufacturing steps to produce each composite layer. The individual layers are then adhesively bonded together in separate operations. These labor intensive operations increase costs and introduce defects at each interface. Additionally, methods to improve multiple hit ballistic and damage tolerance properties, such as Kevlar through-thickness stitching, are not possible using multi-step fabrication methods. The cost and performance issues represent significant obstacles to the insertion of polymer composites technology for Army After Next (AAN) applications. Cost-effective manufacturing techniques that also improve quality and performance must be developed in order to exploit the advantages of multi-functional composite integral armor in Army Applications. Composite integral armor has been identified as a candidate material system for developing combat ground vehicles [1] due to their low density, high stiffness to weight ratio, improved signature management, and corrosion resistance. The composites used in the CAV-ATD had an aerial density 56% and 46% lower than comparable Al and Ti structures respectively [1]. CIRTM/DEA dramatically improves the fabrication of composite armor by eliminating the separate processing and joining steps. Furthermore, new composite structures can now be produced including stitched structures with improved ballistic response (Figure 1b). This new capability is being evaluated for Army applications (Crusader) and may be considered for Future Combat Systems.

Vacuum assisted resin transfer molding (VARTM) processes have been proven to be cost effective manufacturing techniques for the production of large composite structures [2,3]. Previously, their use has been limited to single resin systems. Traditional VARTM processes therefore are not capable of single-step production of composite integral armor materials that require different resins for multi-functionality. CIRTM is a new manufacturing technique developed by the Army Research

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Lab and The University of Delaware Center for Composite Materials which enables the user to manufacture multi-layer hybrid composite parts in a single processing step. CIRTM is facilitated through the use of an appropriate separation media which must not only isolate the individual resins, but also form strong and durable bonds upon cure. Figure 2 schematically shows the CIRTM process. The setup is similar to the Seemann Composite Resin Infusion Molding Process, which is a type of VARTM process [4]. Two resins are simultaneously injected on either side of the preform. The high permeability distribution media facilitates rapid flow along the length and width of the part. The individual resins then flow through the thickness of the preform and are subsequently cured to form the multi-layer composite structure.

For success, the individual resins must not mix upon processing and, thus, techniques that maintain resin separation are critical to the CIRTM process. Additionally, upon cure, the layers must be well bonded to facilitate structural load transfer. Many approaches have been evaluated which can maintain resin separation and promote strong durable bonds between the layers. One promising technique selects separation materials that enable diffusion and cure of the reactive monomers in the separation layer (Figure 2) which results in a diffuse interphase region. The DEA method of interface design provides superior properties since the bonding is accomplished through molecular entanglements that occur in the semi-interpenetrating network which is formed upon diffusion and subsequent curing. The selection criteria for appropriate matrix resins and separation materials must consider compatibility, reactivity, diffusivity, and processing requirements.

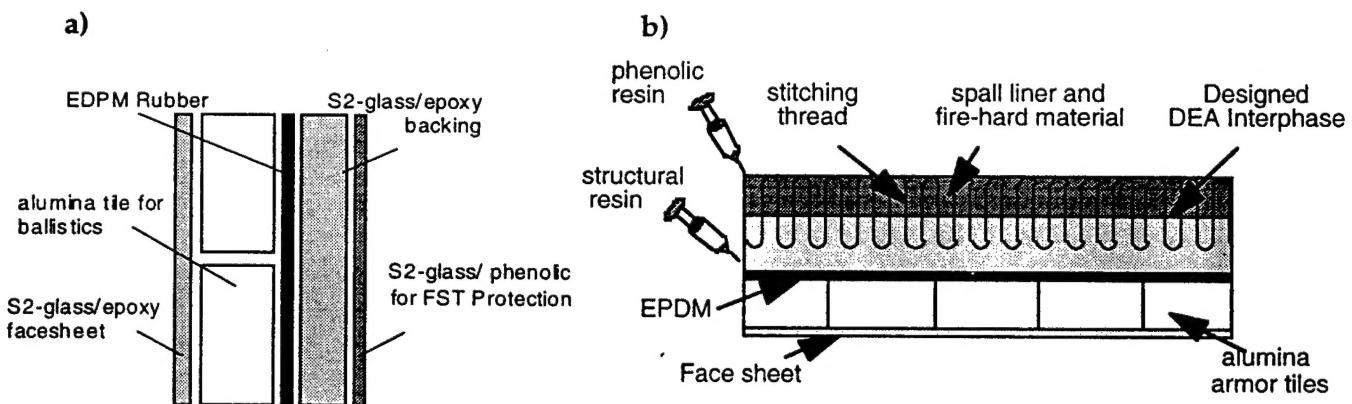


Figure 1. Composite integral armor. a) traditional bonded multi-layer approach. b) CIRTM approach with preform stitching.

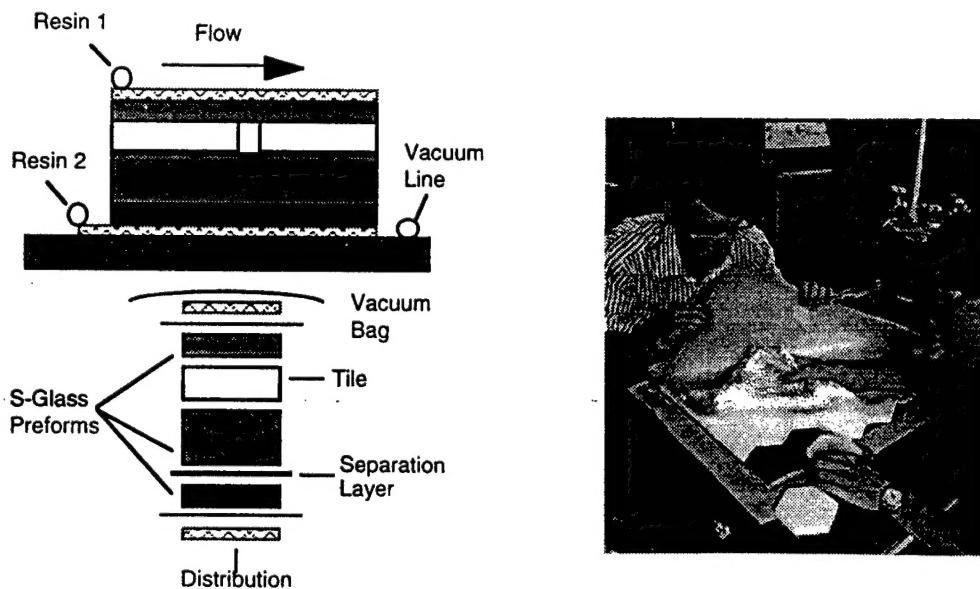


Figure 2. Schematic and photograph of CIRTM preform design and fabrication.

2. Approach

2.1 Separation Layer Design

Certain thermoplastic films have been shown to be excellent separation layers in cases where diffuse interphases are formed [5-8]. For this discussion, we will focus on the diffusion and reaction of epoxy systems into polysulfone thermoplastic separation layers. Similar methodologies can be applied to other thermoset-thermoplastic candidate pairs. The fundamental mechanisms of thermoset-thermoplastic diffuse interphase formation have been studied using theoretical modeling and innovative characterization techniques [5-8]. The DEA approach relies on diffusion of thermoset monomers into fully polymerized thermoplastic materials. Two issues must be considered when selecting materials for the DEA process: compatibility and kinetics. Compatibility is a necessary condition for the thermoset-thermoplastic systems to exhibit interfacial mixing prior to cure. Since the thermoset monomers have molecular weights which are significantly lower than thermoplastic monomers, they can be treated as solvents. In this case, compatible pairs can be chosen by matching solubility parameters (δ) calculated using group contribution techniques [9]. While not formally rigorous, these methods enable rapid screening and down-selection of candidate pairs. The scheme separates individual contributions to the overall solubility parameters from the molecular species in each repeat unit. Values for these contributions have been tabulated for many species [9] and can be used to determine the solubility parameter for the polymer pairs. Compatible polymers are characterized by solubility parameters that are closely matched. It has been found that polysulfone is very compatible with epoxy and amine monomers [5,6] using this approach.

In addition to thermoset-thermoplastic thermodynamic compatibility, the kinetics of diffusion and curing reactions must be considered when selecting materials for DEA type separation layers. The diffusion must be rapid enough to permit significant penetration of the thermoset into the thermoplastic, yet must cease prior to complete permeation of the thermoplastic film by the thermoset. Also, the thermoset must react in the presence of the thermoplastic in order to form an interpenetrating network. Careful characterization of the diffusion and cure reaction processes can provide data to be used in quantitative models of interphase formation to optimize materials selection and CIRTM process parameters. The characterization of thermoset diffusion in thermoplastics is a difficult task. In our laboratories, a novel *in situ* infrared spectroscopy technique is used to quantify diffusion of reacting thermoset monomers in thermoplastic films. The details of this method can be found elsewhere and some results of interest are presented here [5,8]. In general, the thermoplastic polymer is coated onto an internal reflection element and placed into a Fourier-transform infrared (FTIR) spectrometer. The thermoset is introduced into the sample cell adjacent to the thermoplastic film. The thermoset diffuses through the thermoplastic film and is tracked by measuring the increasing absorbance of bands associated with diffusion. Then, the absorbance data is reduced by fitting the data to a suitably chosen diffusion model. Furthermore, since the technique is sensitive to the molecular changes occurring in the sample curing reactions can be monitored simultaneously with diffusion.

Figure 3 shows results from a FTIR diffusion-reaction measurement performed for an epoxy-amine thermoset resin diffusing into polysulfone at 80°C. The points represent normalized absorbance values for two chemical species on the epoxy monomer: the aromatic CH stretch (1510 cm^{-1}), and the epoxide ring asymmetric stretch (912 cm^{-1}). The increase in absorbance of both bands clearly indicates the diffusion of the epoxy into the polysulfone. Furthermore, the eventual decrease in the epoxide ring band demonstrates that the epoxy-amine curing reaction will proceed in the presence of the polysulfone. The solid lines on the graph are predictions from a diffusion-reaction model that relates processing conditions to composition in the thermoset-thermoplastic diffuse interphase. The excellent agreement indicates that the model is capable of capturing both diffusion and reaction effects during the process. These models can be used to optimize the size of the diffuse interphase as a function of materials selection and processing conditions. Similar approaches are taken to determine optimum processing conditions for effective separation of CIRTM resins and maximum bond performance.

2.2 Flow Considerations

The goal of understanding the parameters that govern the flow in CIRTM was met using a one-dimensional flow simulation model. In CIRTM, as the resins fill the two layers in the mold two pressure profiles develop. These profiles are determined by the ratio of the permeability of the preform to the viscosity of the resin. Since the two ratios are different, two different pressure profiles develop in the top and bottom layer. When this occurs, a pressure gradient forms in the transverse direction and it drives the transverse flow. The model also showed that the amount of transverse flow increases rapidly until it reaches a steady state point. All of the results from this model qualitatively matched ones from a finite element model. The finite element model allowed measuring the amount of transverse flow and determining the importance of the transverse permeability and the effect of part length on the transverse flow. The model also relaxed the assumption of

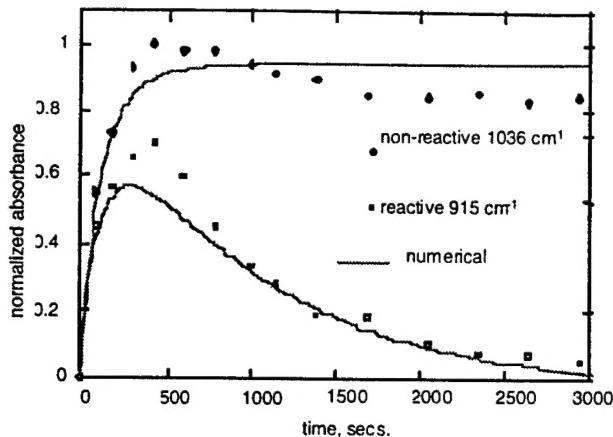


Figure 3. Normalized absorbance from FTIR diffusion-reaction experiment. Solid lines are model predictions.

linear pressure profile in each half of the mold. It showed that a transverse permeability seven orders of magnitude smaller than the in-plane permeability is needed to reduce the transverse flow to less than 1% of half the mold size. In practice, it is almost impossible to find a preform material with this property. Additionally, the finite element code proved that increasing the part length, and therefore the distance that the resin must travel, increases the amount of transverse flow. As in the one-dimensional model, the amount of transverse flow seems to eventually reach a steady state situation but only after a significant amount of mixing has occurred. Overall the results from the two models agree qualitatively and they also agree with preliminary experiments conducted in the lab. In order to use the co-injection process for large structures it is necessary to use a completely impermeable separation layer. This will completely eliminate transverse flow. For smaller scale applications, the results presented in this study provide useful guidance for selection of resin and preforms to minimize transverse flow.

2.3 Fabrication

A distinct advantage of the CIRTM process is the ability to include all of the composite armor elements in a single preform assembly, including various fiberglass fabrics, an elastomer layer, and ceramic alumina tile (Figure 2) [10,11]. At dissimilar material interfaces (e.g. phenolic-epoxy, urethane-epoxy) a separation layer must be used. Here, the separation layer consisted of polysulfone film and epoxy-film adhesives that have been shown to produce DEA bonds with outstanding properties. High permeability distribution media is placed on either side of the preform to enable rapid resin flow in lateral directions prior to through thickness preform infiltration.

Appropriate selection of resin cure cycle is an important challenge presented by CIRTM. To maintain process flexibility is desired to design cure cycles that result in full cure of all of the injected resins. Often, these cure cycles are complex and an understanding of the cure kinetics for each resin is essential to ensure proper cure of the resin materials. Towards this end, empirically derived cure kinetics models for the resins that are presently employed in the CIRTM have been derived. As an example, if Dow Derakane 411-350 vinyl ester and BP J2027/L phenolic are to be used as the structural and FST components in the armor respectively, the following process cycle would be used. To facilitate room temperature cure of the vinyl-ester resin, an organic peroxide initiator (Trigonox 239A) and an accelerator (cobalt naphthalate) would be added to the resin before infusion. Similarly, a catalyst (Phencat 381) would be added to the phenolic. Then, both resins would be injected into the preform at room temperature. The part is then heated to 60°C for four hours to cure the phenolic and then 95°C for four additional hours to cure the epoxy adhesive/polysulfone separation layer and post-cure the vinyl ester. Custom process cycles have also been derived for other resins that ensure complete cure.

3. Results

Using the procedures outlined above, CIRTM has been used successfully to simultaneously process numerous resin combinations. These have included vinyl ester/phenolic, epoxy/phenolic, epoxy/urethane, and elastomer/epoxy resin combinations. In all cases, excellent composites were produced with no mixing of the individual resins. Figure 4a shows a micrograph of an CIRTM composite in the interphase region that demonstrates the quality of each laminate. Furthermore, we have used CIRTM to process stitched laminates with superior damage tolerance compared to baseline composite integral armor structures (Figure 4b).

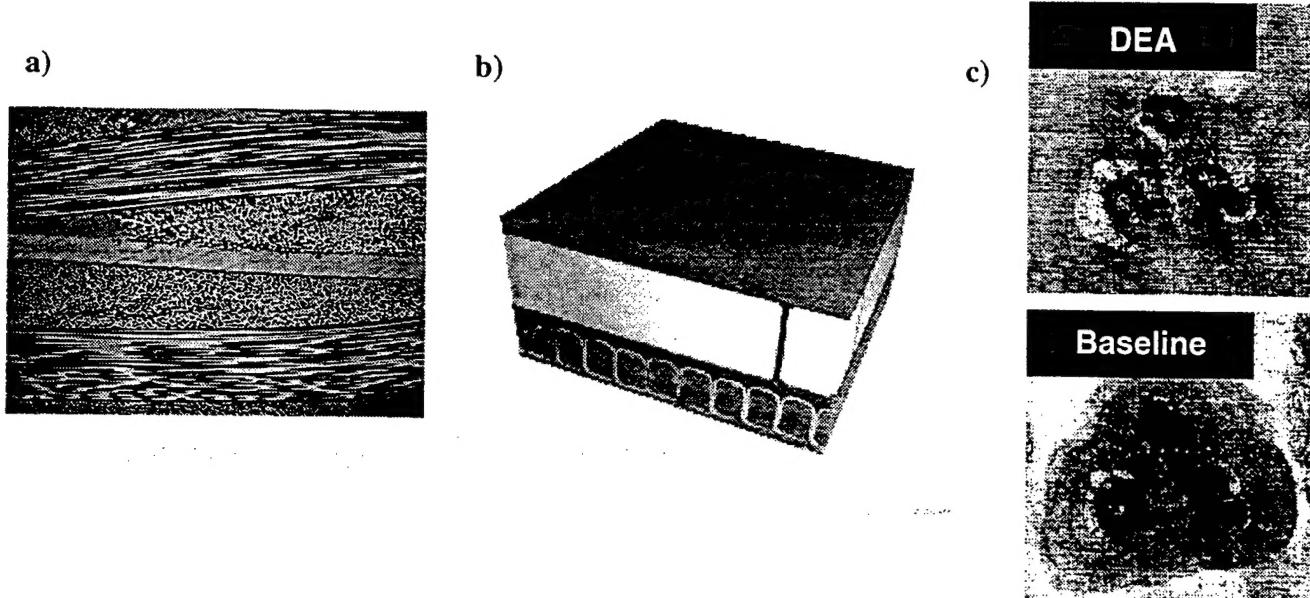


Figure 4. (a) Micrograph of CIRTM composites near separation layer. (b) Photograph of stitched integral armor. (c) Ultrasonic C-scans of impacted composite plates.

The mechanical properties of the CIRTM composites and the DEA separation layer are excellent. Tables 1 and 2 show the short beam shear (SBS) strength and the mode one fracture toughness respectively. The composite mechanical properties formed using the CIRTM processes are equivalent or superior to ones provided by separate assembly and bonding operations. In some cases the interfacial strength and toughness approaches or exceeds that of either parent material. Preliminary tests show that DEA bonds exhibit superior resistance to delamination during ballistic impact. Figure 4c shows ultrasonic c-scans of impacted DEA and baseline bonded panels. The reduced delamination in the DEA parts illustrates the improved ballistic impact resistance compared to baseline materials. Efforts are continuing to provide insight into optimization of CIRTM/DEA processes.

Table 1. Short beam shear (SBS) strengths.

Resin	Separation Layer	Resin	SBS Strength Mpa (lbs./in ²)
Dow Vinyl ester 411-350	none	Dow Vinyl ester 411-C50	37.0 +/-0.83 (5373 +/-121)
BP Phenolic J2027	none	BP Phenolic J2027	22.6 +/-0.81 (3279 +/-118)
Dow Vinyl ester 411-350	secondary bond	BP Phenolic J2027	23.5 +/-1.61 (3415 +/-233)
Dow Vinyl ester 411-350	Epoxy film adhesive	BP Phenolic J2027	30.8 +/-1.37 (4472 +/-198)
Dow Vinyl ester 411-350	Epoxy-phenolic film adhesive	BP Phenolic J2027	23.8 +/-1.17 (3446 +/-170)

Table 2. Fracture toughness (G_{Ic}) results.

Resin	Separation Layer	Resin	Mode I Fracture Toughness (J/m^2)
Dow Vinyl ester 411-350	none	Dow Vinyl ester 411-C50	1220 +-82
BP Phenolic J2027	none	BP Phenolic J2027	727 +-59
Dow Vinyl ester 411-350	secondary bond	BP Phenolic J2027	715 +-121
Dow Vinyl ester 411-350	Epoxy film adhesive	BP Phenolic J2027	859 +-200
Dow Vinyl ester 411-350	Epoxy -Phenolic film adhesive	BP Phenolic J2027	938 +-73

4. Conclusions

From first principles to ballistic testing of optimized composite armor panels, ARL and UD-CCM have invented and demonstrated two leading edge technologies which merge to enable improved single and multiple-hit ballistic performance, FST performance, and post-ballistic structural/durability performance in composite armored systems. Added benefits demonstrated include improved sustainability by effectively increasing the critical damage size for subsequent service and decreasing the growth of existing damage thereby significantly reducing repair requirements. The interphase region formed in the CIRTM/DEA process provides a toughened interlayer for optimized load transfer and fracture toughness between dissimilar materials and eliminates the need for secondary bonding. Several studies have been performed which optimize the procedures for co-injection and which optimize the development of strength and toughness in the interphase region.

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